I. CATIONIC POLYMERIZATION OF BUTADIENE BY STANNIC CHLORIDE

II. POLYURETHANS AND POLYESTERS FROM BUTENEDIOLS

BY

CHARLES HERBERT YOUNG

A.B., Columbia University, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE UNIVERSITY
OF ILLINOIS, 1950

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PART I

CATIONIC POLYMERIZATION OF BUTADIENE BY STANNIC CHLORIDE

INTRODUCTION

Many attempts have been made to prepare a synthetic polymer which would have the characteristics of natural rubber, which is a linear polyisoprene having a *cis* configuration around the internal double bonds. One of the most useful of these synthetic rubbers, "Butyl" rubber, is a copolymer of isobutylene and butadiene in which the latter is present in amounts up to 20 per cent. The polymerization is carried out at a low temperature in the presence of a Friedel-Crafts type catalyst, usually aluminum chloride, and yields a high-molecular weight, substantially linear polymer.

This investigation of the polymerization of butadiene, with stannic chloride as catalyst, was undertaken in an attempt to prepare a soluble polybutadiene at a low reaction temperature, and to determine the effect of the catalyst on such factors as viscosity, per cent 1,4-addition, and solubility. The results were also compared with those of similar researches which employed aluminum chloride, boron trifluoride-etherate and chlorosulfonic acid as catalysts. The initial experiments were at —75°, but it was found necessary to raise the temperature to 0° or higher in order to obtain any reaction.

DISCUSSION OF RESULTS

Stannic chloride was found to be an active catalyst for the polymerization of butadiene at 30 and 50°, but not at 0 and —75°. The reaction gave erratic and often irreproducible results, and was very susceptible to impurities, especially moisture.

In the conversion range from 10 to 40 per cent soluble, tacky elastomers of low molecular weight were often obtained. Viscous liquid polymers were formed at conversions below 10 per cent, while above 40 per cent inelastic products of low solubility were obtained. Moisture accelerated the reaction, and was also a major factor in the lack of reproducibility. Before appreciable reaction

occurred there was an induction period of at least forty-eight hours, which increased as more anhydrous reaction conditions were obtained, or with increased dilution of the monomer, or lower catalyst concentration. The effect of other variables, such as solvent and reaction time, was also studied. In general, the maximum conversion obtained was 60-70 per cent, with further reaction leading to greater cross-linking. However, when an essentially anhydrous procedure was employed a maximum conversion of 29 per cent was obtained, even after twenty-one days. In these experiments the induction period was greater than five days.

The molecular weight of soluble stannic chloride-catalyzed polybutadienes was very low as indicated by intrinsic viscosity measurements. Values from 0.1 to 0.3 were usually obtained. The per cent of 1,4-addition in the polymer was found to be in the same range as in similar polymers made using chlorosulfonic acid or aluminum chloride as catalyst (1).

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Part II

POLYURETHANS AND POLYESTERS FROM BUTENEDIOLS

INTRODUCTION

Although many varieties of polymers have been prepared in the last few decades, there has been little work on the effect of small structural differences on the properties of the polymers. The present work represents a continuation of the research undertaken in this laboratory (1) to study the effect of carbon-carbon single, double, and triple bond linkages in polymers whose structure was otherwise identical.

In the case of the double bond linkage, both *cis* and *trans* isomerism are possible. Both *cis* and *trans*-2-butene-1,4-diol have been made and converted to polyurethans by reaction with hexamethylene diisocyanate, and to polyesters by reaction with sebacic acid. The second order transition temperatures and X-ray diffraction patterns of the polymers were determined in order to study the degree of crystallinity within the molecule. Mixed polyurethans obtained by the reaction of the diisocyanate with mixtures of each of the two diols with 1,4-butanediol were prepared in order to calculate values for the heat and entropy of fusion. These values give further indication of the stiffness of the polymer chains.

DISCUSSION OF RESULTS

The *cis* and *trans* isomers of 2-butene-1,4-diol have been prepared and converted to polyurethans by reaction with hexamethylene diisocyanate, and to polyesters by reaction with sebacic acid. The synthesis of the *cis* diol was accomplished in 80 per cent yield by the low-pressure, Raney nickel-catalyzed hydrogenation of 2-butyne-1,4-diol. The *trans* diol was prepared in 66 per cent overall yield from butadiene through the 1,4-dibromo and 1,4-diacetoxy compounds.

The polyurethans and polyesters from the *cis* diol melted lower than the corresponding *trans* compounds, but otherwise there was little difference in the properties of the polymers which could be attributed to *cis-trans* isomerism. This was indicated by X-ray

diffraction patterns, second order transition temperatures, and heat and entropy of fusion calculations. All of the polymers exhibited a comparable degree of crystallinity which was less than that found in the analogous saturated compounds. Entropy and second order transition temperature determinations showed that the olefinic polymers were stiffer than the saturated polymers, and that the amorphous areas assumed stability at a higher temperature. The butenediol polymers were not as stiff and rigid as the butynediol analogues, but rather were intermediate between them and the saturated compounds.

The infrared spectra showed the presence of the *cis* or *trans* unsaturation, but all of the curves were very similar. In polymers with increasing olefinic content the carbon-carbon double bond absorption increased, while the single bond absorption decreased or vanished completely.

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VITA

The author was born in New York City on May 19, 1923. He attended public schools in Charleston, West Virginia, Rochester, New York, and Toledo, Ohio, where he was graduated from Scott High School in June, 1939. He matriculated at Hamilton College, Clinton, New York, for two years and then transferred to Columbia University, from which he was graduated with the degree of Bachelor of Arts in February, 1943. From that date until January, 1946, he was employed as a research chemist by Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation, South Charleston, West Virginia. He entered the graduate school of the University of Illinois in September, 1946. From February, 1947, to June, 1950, he held a Special Research Assistantship in chemistry which was supported by the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.